

LOCATION OF THE HYDROCARBON POTENTIAL DURING COAL PYROLYSIS: IMPLICATIONS ON THE CHEMICAL MODELLING

E. Langlois, R. Michels, M. Elie, L. Mansuy, O. Ruau and P. Landais

CNRS-CREGU, BP 23, 54501 Vandoeuvre Cedex, France.

Key words: artificial maturation, asphaltenes, resins, hydrocarbon generation.

INTRODUCTION

The modelling of hydrocarbon generation and the understanding of the compounds distributions (i.e. correlations on the basis of geochemical fingerprints) necessitate to establish genetic relationships between the kerogen and the corresponding rock extracts and oils (containing free hydrocarbons, but also the polars). These genetic relationships imply that the fate of the hydrocarbons in the organic system during maturation is known qualitatively (hydrocarbons distribution) and quantitatively (hydrocarbons potential). Hydrocarbons distributions and potential must therefore be defined for each organic fraction: the kerogen, the asphaltenes and resins as well as the free hydrocarbons. This implies a careful study of the composition of each fraction in regards to the degree of maturation and their respective behavior in the chemical maturation processes involved.

A precise study on the geochemical fingerprint and hydrocarbon potential of each organic fraction has been performed on an artificially matured coal. The combination of GC-MS and Py-GC-MS accompanied by semi-quantitation calculations allowed to identify the hydrocarbons distribution in each phase, to relate it to the respective hydrocarbon potential, and this for each maturation level.

EXPERIMENTAL

Sample. The sample used in this study is an immature homogeneous vitrinite-rich coal from the Mahakam delta (Indonesia) of low ash content (H/C=0.97; O/C=0.21; HI=335 mg/g) This sample has been widely studied and numerous data on both natural and artificial maturation are available^{1,2}.

Artificial maturation. 1 gram aliquots of the coal were loaded in gold cells (L=5cm; I.D.=1cm) under inert atmosphere. Isothermal confined pyrolysis runs were conducted at temperatures ranging from 250°C to 400°C by 10°C steps during 72h at 700bars pressure. The procedure and the pyrolysis apparatus are described elsewhere³. Detailed geochemical data on this series of maturation are available².

Collection of the different fractions. After pyrolysis, bitumen were extracted with chloroform at 60°C during 45 minutes. Asphaltenes were precipitated with 40 volumes of n-heptane at 40°C during 15 minutes. The maltene fraction, soluble in the n-heptane was fractionated into saturates, aromatics and resins using microcolumn liquid chromatography. Mass balance allowed quantitation of each fraction.

Gas Chromatography-Mass spectrometry (GC-MS). Saturates and aromatics were analyzed by gas chromatography-mass spectrometry (HP 5890 Serie II GC coupled to a HP 5971 mass spectrometer), using an on-column injector, a 60 m DB-5 J&W, 0.25 mm i.d., 0.1mm film fused silica column. The temperature program was 40 to 300°C at 3°C/min followed by an isothermal stage at 300°C for 15 min (constant helium flow of 25 cm/s)

Flash pyrolysis-Gas Chromatography-Mass Spectroscopy(Py-GC-MS). Py-GCMS of asphaltenes, resins and extracted residual kerogen were performed with a CDS 2000 pyroprobe. Samples were loaded in quartz tubes and heated at 620°C for 15s. The GCMS characteristics and temperature program were the same as described above. Flash pyrolysis yields were estimated by mass balance.

Semi-quantitation of the Pyrograms. The comparison of the absolute hydrocarbon potential of the asphaltenes, resins and residual kerogen in relation to the free hydrocarbons is very difficult because any quantitation technique has its limits and the actual quantitation of the source in the initial sample is impossible (it would require the quantitation of each functional group suspected to be the source of free hydrocarbons). However, the combination of the different techniques used in this work allows a relative mass balance to be calculated. The saturates potential has been assessed using a semi-quantitative approach combining Py-GC-MS yields, chromatogram integration, confined pyrolysis yields, the final value being expressed in mg of coal before pyrolysis. This method allows a relative comparison of the saturates potential of each fraction standardized to the initial coal potential.

RESULTS AND DISCUSSION

Table 1 gives the yields of hydrocarbons, asphaltenes, resins obtained after confined pyrolysis of Mahakam coal. The maximum of resins generation is reached at 320°C, while that of the asphaltenes occurs at 330°C. The maximum of C15+ saturates is reached at far higher temperature (360°C) while the C15+ aromatics are released over a large range of temperatures.

As far as the C15+ saturates are abundant in this sample and have a very characteristic pattern, the n-alkanes distribution will be used as tracer of hydrocarbons release in this study. Figure 1 gives an example of the m/z=57 chromatograms obtained for the free C15+ saturates (GC-MS), the resins, asphaltenes and residual kerogen (Py-GC-MS) obtained after confined pyrolysis at 260 and 350°C.

At a given maturation temperature, the aliphatic chain distribution in the resins pyrograms is quite similar to the free saturates chromatograms. The same odd-alkanes predominance is characteristic. On the contrary, the aliphatic distribution is different in the asphaltenes as well as in the residual solid: the odd alkanes predominance is less pronounced, and the maximum of the distribution is shifted towards the lower molecular weight hydrocarbons for the residual kerogen. An increased apparent maturity is therefore observed in the following order: the free saturates and resins look less mature than the asphaltenes which look less mature than the residual kerogen. These results show that although the coal has experienced the same thermal history, the compounds distribution in each organic phase does not reflect the degree of maturation in the same manner.

The flash pyrolysis yields of the Mahakam extracted residual kerogen, asphaltenes and resins have very different values and evolutions with maturation. Solid yields decrease from 40% (initial sample) to about 10% at 390°C, the main cause being the decrease of the oil potential. For asphaltenes and resins the pyrolyzate yields are

more important (about 60 and 80% respectively), and increase of about 10 to 15% with maturity, a behavior quite different from that of the resid.

Figure 2 shows the evolution of the saturates potential of each fraction (as defined in the experimental section) as a function of maturation. At the beginning of the maturation process the kerogen, of course, contains the most important amount of aliphatic hydrocarbons. In the mean time, the generation of polars is dominant. Consequently, the saturates potential of the kerogen decreases, while that of the polars increases. The decrease of the saturates content in the kerogen cannot be totally explained by the fairly low increase of the amount of free saturates (neither by the generation of the aromatic fraction that does not contain high amounts of long-chain alkyl-aromatics). A great part of the saturates potential is therefore transferred to the polars.

After the maximum of polars generation has been reached (330°C), the saturates potential calculated for the polars and the residual kerogen is fairly similar, and both contribute to the generation of the increasing amounts of free saturates. However, a look at the n-alkanes distribution within each of these fractions shows major differences between the polars and free saturates on one side and the residual kerogen on the other. This latter is highly dominated by lighter molecular weight n-alkanes, while the others still display a strong contribution of n-paraffins with a marked CPI. This feature suggests that the polars are mainly a source of C15+ n-alkanes at T>330°C, while the residual kerogen rather contributes to the generation of the C7-C14 n-alkanes. This picture is still valid at temperatures up to 360°C. From 360°C and higher, secondary cracking of the generated alkanes occurs, and the n-alkanes distribution in the various fractions is tending to homogenize (i.e. getting lighter), thus increasing the difficulty to properly identify the various sources of n-alkanes.

It has been shown earlier that the asphaltenes, resins and residual kerogen do not bear the same geochemical signature (i.e. alkanes and biomarkers distributions) at a given maturation step, the signature being the "most mature" for the solid and the "less mature" for the resins. Correlatively, their respective contribution to the generation of the free saturates, in terms of quality (hydrocarbon distribution) and timing (dominant hydrocarbon source) are different.

Thus, at the beginning of maturation (stages 250-330°C), a part of the kerogen (and its corresponding alkanes potential) is converted into the polar fraction in relation to the removal of low energy bonds (such as oxygen bonds). In a following maturation stage (330-360°C), the residual kerogen and the polars are thermally degraded and do not generate the same hydrocarbons.

CONCLUSIONS

The use of artificial maturation allows to compare the yields and composition of the free hydrocarbons, asphaltenes, resins and residual kerogen obtained from the pyrolysis of an immature coal. An integrated study of the various fractions gives interesting information concerning the evolution of the hydrocarbon potential of each phase and of the compounds distribution. The sample being characterized by a high n-paraffin content with a very typical distribution, the alkanes were used to discuss this aspect. It could be shown that:

- a great part of the hydrocarbon potential initially present in the kerogen, is progressively transferred into the polars (bitumen generation phase). At the mean time, low amounts of saturates are generated. Once the thermal degradation of asphaltenes and resins has been reached, both phases together with the residual kerogen contribute to the generation of free hydrocarbons.

- however, the distribution of the hydrocarbons released are different between the residual kerogen, asphaltenes, resins and free hydrocarbons. As a consequence, the relative maturity indicated by geochemical markers (biomarkers, compounds distribution) are different in each fraction.

It has been shown elsewhere^{4,5,6} that the polars have a different reactivity from the residual kerogen. Especially their interaction capabilities with the surrounding medium and their interaction with water imply that they play a specific role in the maturation process. This study shows that polars have also specific structural characteristics compared to the residual kerogen. As a consequence, the hydrocarbon release depends on a great part from the chemical reactivity of the polars, both quantitatively and qualitatively (the free hydrocarbons distribution mainly derives from the resins). This work suggests that the modellisation of hydrocarbons generation needs to take into account the specific behavior of the polars.

REFERENCES.

- (1) Monthieux M., Landais P., Monin J. C. *Org. Geochem.*, **1985**, *8*, 275-292.
- (2) Landais P. and Gérard L. *Coal geology*, **1996**, *30*, 285-301.
- (3) Landais P., Michels R. and Poty B. *Journal of Anal. and Appl. Pyrolysis*, **1989**, *16*, 103-115.
- (4) Mansuy L., Landais P. and Ruau O. *Energy Fuels*, **1995**, *9*, 691-703.
- (5) Mansuy L. and Landais P. *Energy Fuels*, **1995**, *9*, 809-821.
- (6) Michels R., Langlois E., Ruau O., Mansuy L., Elie M., and Landais P. *Energy Fuels*, **1996**, *10*, 39-48.

FIGURES AND TABLES

T(°C)	Asphaltenes	Resins	Saturates
250	1.7	3.2	0.3
260	1.9	3.1	0.4
270	2.1	4.1	0.5
280	2.0	4.1	0.4
290	2.1	5.6	0.8
300	2.7	6.4	1.0
310	3.1	8.6	1.5
320	3.8	9.0	1.8
330	4.8	8.7	2.5
340	2.2	7.3	3.1
350	1.6	6.2	4.6
360	1.0	6.2	5.8
370	1.0	3.2	3.3
380	0.6	1.9	2.5
390	0.5	1.1	1.8
400	0.3	0.8	1.0

Table 1: Asphaltenes, resins and saturates yields (in mass percent of initial coal) obtained after confined pyrolysis of Mahakam coal.

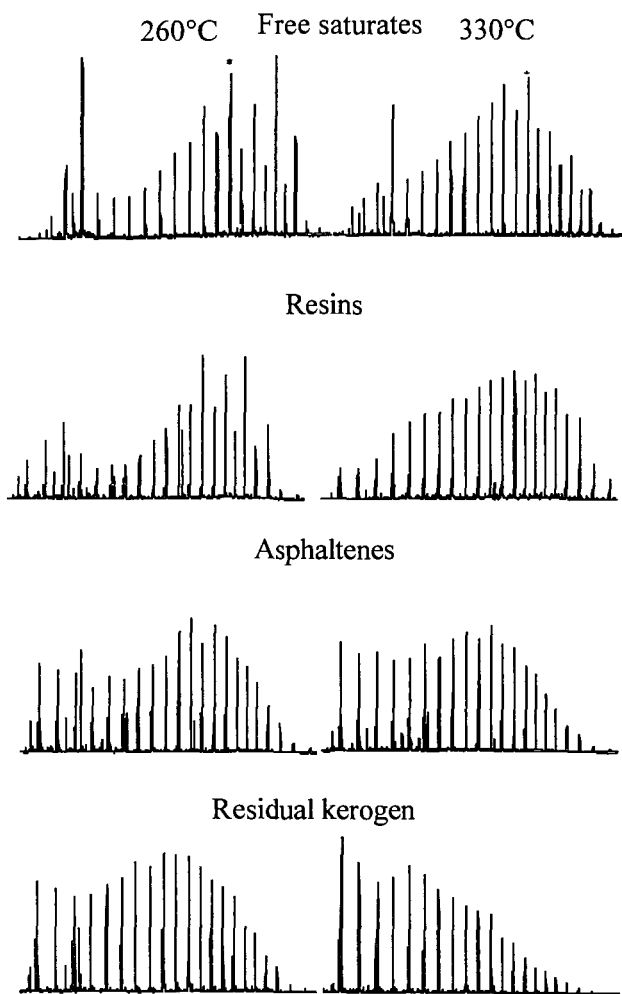


Figure 1: Comparison of the n-alkanes distributions ($m/z=57$; C17-C35 range, the star indicating nC27) observed in the free hydrocarbons (GC-MS) the resins, asphaltenes and residual kerogen (Py-GC-MS) generated from the Mahakam coal during confined pyrolysis at 260 and 330°C.

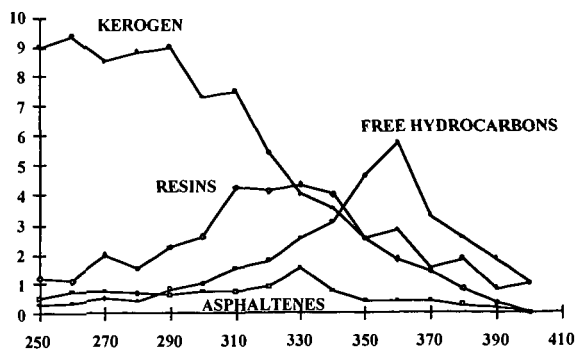


Figure 2: Evolution of n-alkanes yields (in weight percent of immature coal) obtained after semi-quantitative calculations based on Py-GC-MS yields, chromatogram integrations as well as confined pyrolysis yields of asphaltene, resins and residual kerogen. These values represent the relative hydrocarbon potential for each phase. Are also plotted the free saturates yields obtained after confined pyrolysis (values also normalized to immature coal mass).